Document No. 1 001 040 Al.

PROCESS FOR SURFACE HARDENING MOLDINGS OF CASTING MATERIAL AS

WELL AS MOLDINGS PRODUCED THEREWITH AND THEIR USE

[Verfahren zur Oberflaechenhartung von Formkoerpern aus

Gusswerkstoff sowie dadurch hergestellte Formkoerper

und deren Verwendung]

Frank Grunow

UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C. February 2003

Translated by: Schreiber Translations, Inc.

<u>Country</u> : Europe

<u>Document No.</u> : EP 1 001 040 A1

<u>Document Type</u> : Publication of application with

search report

<u>Lanquage</u> : German

<u>Inventor</u> : Frank Grunow

<u>Applicant</u>: Federal-Mogul Burscheid Ltd.,

Burscheid, Federal Republic of

Germany

<u>IPC</u> : C21D 5/04, C23C 8/26

<u>Application Date</u> : November 11, 1999

<u>Publication Date</u> : May 17, 2000

<u>Foreign Language Title</u> : Verfahren zur Oberflaechenhartung

von Formkoerpern aus Gusswerkstoff

sowie dadurch hergestellte

Formkoerper und deren Verwendung

English Title : PROCESS FOR SURFACE HARDENING

MOLDINGS OF CASTING MATERIAL AS

WELL AS MOLDINGS PRODUCED THEREWITH

AND THEIR USE

Process for Surface Hardening Moldings of Casting Material as well as Moldings Produced therewith and their Use

Process for surface hardening a molding of metastable solidified iron-carbon casting material, wherein the process comprises at least the steps of: heating the molding in a decarbonizing atmosphere, cooling the molding, if required tempering the molding, and heating the molding in a nitrogenemitting medium. The invention also concerns the molding produced with the process as well as its use.

/2

Description

[0001] The invention concerns a process for surface hardening moldings of metastable solidified iron-carbon casting material as well as the moldings produced with the process and also their use.

[0002] The hardening of the surface of moldings of solidified iron-carbon casting material (such as, for example, piston rings, driver rods, contact surfaces of tooth flanks in toothed wheels, etc.) is of enormous economic importance with regard to the abrasion resistance of these moldings. In the state of the art are know different processes for increasing the abrasion

¹ Numbers in the margin indicate pagination in the foreign text.

resistance of these moldings. For example, galvanically isolated hard chrome layers and flame sprayed molybdenum layers are used as abrasion protective layers. However, these processes are complex and cost intensive.

[0003] It has been shown that nitrocarburized moldings such as, for example, piston rings for use in spark ignition engines or diesel motors appear to be equal or better with a view to the abrasion resistance than the moldings provided with an abrasion protection layer of hard chrome. With regard to the burning trace security, the nitrocarburized moldings appear to be comparable to the moldings that are provided with an abrasion protective layer of molybdenum.

of hardened metastable cast iron with an at least partially martensite-like structure that contains a graphite chemical deposition and is nitrated in a volume field that extends from the surface into the interior of the molding. The outer field volume, with the exception of finely dispersed graphite depositions, is essentially free of graphite.

[0005] According to the technical teaching disclosed in

DE 34 07 010 C2, the nitriding of the molding must take place
before the hardening by heat treatment of the cast iron. The
execution of the nitriding of the body before heat treatment
leads to a suppression of a graphite disposition that is not

finely dispersed in the molding, which occurs necessarily during the heat treatment of the molding without previous nitriding.

[0006] Extremely disadvantageous of the molding produced according to DE 34 07 010 C2 is that the nitriding field volume, that is, the surface edge layer of the molding, in which the nitride formation has occurred, has a very small depth with respect to the surface. In the nitriding, the nitrogen diffuses from the surface of the molding into the interior of the metastable solidified cast iron and forms iron carbonitrides together with the iron carbides or iron mixed carbides. These iron carbonitrides have a considerably better thermal stability when compared to the iron carbides or iron mixed carbides.

[0007] After nitriding, the obtained hard and brittle cast molded blank must be subjected to a carbide dissociation annealing so that the casting material can be processed. The graphite deposition is prevented on the surface edge layer in which the iron carbonitrides are due to the previously mentioned greater thermal stability of the iron carbonitrides.

[0008] A mechanical post-processing, which can take place after carrying out the nitriding and carbide dissociation annealing, if required, is practically impossible since in this way the surface edge layer containing the nitrides is partially or completely removed. The thickness of the nitrified surface edge layer is generally 100 mm. In the mechanical post-

processing of the interior of the nitrided cast molded blank, the inner non-nitrided core area of the molding, which has deposited graphite as a consequence of the carbide dissociation annealing, comes therefore again to the surface of the molding.

[0009] Since the cast pieces have regularly large tolerances, a mechanical post-processing of the cast molded blank is only necessary when the end product must have a high fitting accuracy. Insofar, no accurately fitting molding provided with a consistent abrasion protective layer could be produced with the process of DE 34 07 010 C2. This is extremely disadvantageous.

[0010] It is an object of the invention to provide a process for producing an abrasion-resistant molding on the basis of a metastable solidified iron-carbon casting material wherein the production of abrasion-resistant and, if required, accurately fitting moldings is possible.

[0011] Another object is the production of an abrasionresistant and if required accurately fitting molding on a basis
of a metastable solidified iron-carbon casting material.

[0012] The object of the invention is attained by providing a process for the surface hardening of a molding of metastable solidified iron-carbon casting material wherein the process comprises at least the steps of:

- (a) heating the molding in a decarbonizing atmosphere,
- (b) cooling the molding,

- (c) if required, annealing the molding, and
- (d) heating the molding in a nitrogen-emitting medium.

<u>/3</u>

- [0013] Under the term "decarbonizing atmosphere" is understood in the sense of the invention any environment that is suitable for reducing the content of deposited graphite in the surface edge layer. The decarbonization can therefore be undertaken in a gas atmosphere or in the plasma.
- [0014] Under a surface edge layer is understood in the sense of the invention the layer located under the surface of the molding, which seen from the surface of the molding extends into the interior of the molding. The depth of the surface edge layer is therefore a length measure that extends vertically with respect to the surface.
- [0015] For example, the decarbonizing atmosphere is formed by the gases that constitute the annealing atmosphere, such as oxygen, water vapor, H_2 , CO, CO_2 , et cetera or mixtures of these. The decarbonizing atmosphere, however, can also consist of CO/CO_2 and N_2 . Of course also other thinned gases can be contained in the decarbonizing atmosphere. Particularly preferred in the sense of the invention is an atmosphere of $CO/H_2/N_2NH_3$.
- [0016] A heating of the casting material pieces in a decarbonizing atmosphere effects an edge decarbonation of the casting material piece, which can be seen well in a broken-away

or sliced-away view. The extent of the decarbonization in the edge layer of the casting material piece, that is, if the carbon content is reduced or is equal to zero, depends upon the applied external conditions (time duration, temperature, type of atmosphere, carbon level in the atmosphere, et cetera). Also the depth of this surface edge layer with reference to the surface depends upon the respectively applied conditions under which the decarbonization reaction is carried out.

[0017] Under a cooling of the molding is understood in the sense of the invention a slow cooling as well as a rapidly occurring cooling (the so-called quenching) of the molding. No martensitic hardening of the molding occurs in a slow cooling. A quenching of the molding, that is, a rapidly occurring cooling of the molding is preferred in the execution of the process of the invention.

[0018] Under a tempering of the molding is understood in the sense of the invention a heat treatment of the molding. A tempering of the molding is not necessarily required. For example, a tempering of the molding can be omitted when a martensitic hardening has not occurred, which can be the case, for example, in a slow cooling of the molding.

[0019] Under a nitrogen-emitting medium is understood in the sense of the invention any medium that is suitable for releasing the nitrogen required in the nitriding or nitridation or

nitrogenizing on the surface edge layer. The released nitrogen diffuses then into the surface edge layer and forms the corresponding nitride compounds.

[0020] The terms nitriding or nitridation or nitrogenizing have the same importance as far as their meaning in the sense of the invention. For reasons of simplicity, the terms nitriding or nitridation will be used in the following.

[0021] The nitriding can therefore take place as a gas nitriding in that, for example, ammonia gas is allowed to dissociate on the surface of the molding. It is also possible to carry out the nitriding in the form of a glow nitriding or ion nitriding or plasma nitriding, in which the nitriding takes place with nitrogen under the influence of a glow discharge. Of course, the nitriding can also be undertaken in a salt bath (for example, by using alkali cyanates, carbonates, or cyanides).

[0022] The nitriding takes place preferably in the sense of the invention in a gas atmosphere or in the plasma.

[0023] In a preferred embodiment of the invention, another process step wherein a processing of the molding takes place is provided in the process of the invention between the process step (c) and the process step (d).

[0024] It is extremely advantageous if the process of the invention allows a processing of the molding before the nitriding. In this way is possible a mechanical post-processing

of the cast molded blank wherein, for example, the casting skin can be removed from the cast molded blank, and a molding rotation or post-processing can be carried out.

[0025] As already mentioned above, the processing of the cast molded blanks of metastable solidified iron-carbon casting material is only possible after carrying out the carbide dissociation annealing.

[0026] In the process of the invention, the decarbonization and the carbide dissociation annealing take place jointly during the step (a).

[0027] The process of the invention allows therefore extremely advantageously a mechanical post-processing of, for example, piston ring molded blanks before carrying out the surface hardening, that is, the nitriding of the surface edge layer. Because of the deep-reaching decarbonization of the surface edge layer, the end product according to the invention, that is, for example, the piston ring after the post-processing and the nitriding on the surface, does not have free graphite but a consistently nitrided surface edge layer without graphite depositions.

[0028] The process of the invention allows as a consequence the production of qualitatively nitrided moldings of metastable solidified iron-carbon casting material with an extremely high performance and which can be accurately fitted with regard to the

post-processing possibility with respect to their geometric measurements. Insofar, extremely abrasion-resistant and accurately fitting moldings of metastable solidified iron-carbon casting material could been produced.

/4

[0029] It is further preferred if the metastable solidified iron-carbon casting material is a malleable cast iron.

[0030] As metastable solidified iron-carbon casting material is preferably used a malleable cast iron that is adjusted in such a way with respect to the carbon content that it solidifies free of graphite. The entire carbon is available therefore, in contrast with the cast iron with lamella and spheroidal graphite, in bonded form as iron carbide. The fracture appearance is therefore not gray but white do to the lack of black graphite.

[0031] This cast, which was unusable in the original state due to its high hardness and brittleness, is heated so that the iron carbide dissociates and graphite is deposited in the form of temper carbon. The molding receives by way of this heat treatment its properties, which are advantageous for the further processing, with regard to toughness and forging properties which have shown to be advantageous in the further processing of the cast moldings.

[0032] When heating the tempered cast in the decarbonizing atmosphere, the carbon is extracted from the surface of the

tempered cast, that is, the partial or complete decarbonization of the surface edge layer takes place on the one hand, and the carbon, which remains in the core of the molding as iron carbide (cementite), is converted into tempered carbon (carbide dissociation annealing) on the other hand.

[0033] Therefore, a steel-like material is available on the surface edge layer. The depth of the decarbonized surface edge layer corresponds to the layer in which the nitrogen can be diffused by the nitriding step (d) so as to be bonded as nitride.

[0034] It is advantageous if the graphite-free area after the mechanical processing of the molding corresponds to about the nitrided layer thickness so as not to extend the decarbonization time excessively.

[0035] As a rule, the carbon content in the surface edge layer increases continuously from the edge or surface to the core of the molding. Therefore, with regard to a mechanical post-processing, it is advantageous if the carbon content amounts in the outermost surface edge layer at least to about 0.15% by weight. At the temperatures that are preferably used in accordance with this invention, a graphite deposition does not occur with a content of up to 1.5% by weight carbon in the moldings. In other words, within a range of about 0.15% by weight to about 1.5% by weight carbon, the carbon is chemically bonded in the surface edge layer in carbide form.

[0036] Furthermore, the tempered cast to be used preferably in accordance with the invention can contain additives in the form of further metals or metal compounds, which are suitable as so-called nitride builders, to which nitrogen entering into the tempered cast by diffusion is bonded as nitride during the nitriding phase. These can be, for example, the metals Al, Ti, V, Nb, Cr, Mo, or W. Other metals or in general other additives can also be contained in the tempered cast.

[0037] It is advantageous when the moldings in step (a) have a temperature lying within a range between about 700°C and about 1200°C. It is also preferred when the temperature lies within a range between about 800°C and about 1100°C, in particular within a range between about 900°C and about 1080°C. It is very preferred if the temperature of the molding in the step (a) lies at about 1050°C.

[0038] It has been shown that, at the temperatures applied in step (a) according to the process of the invention, it is extremely advantageous if the carbide dissociation annealing as well as also the defined decarbonation of the surface edge layer take place simultaneously. It is assumed that, at the temperatures of the carbide dissociation annealing applied according to the invention, the diffusion speed of the elements is great and the decarbonization of the surface edge layer occurs very rapidly. The conditions are therefore adjusted so that the

decarbonization occurs more rapidly than the graphite deposition, so that no hollow spaces are produced on the surface edge layer. The carbon content in the surface edge layer is clearly lower after carrying out the step (a) and no graphite deposits up to a depth of 1.5 mm with reference to the surface of the molding.

[0039] A small content of iron carbide in the decarbonized surface edge layer of less than 5% with reference to the content of iron carbides before decarbonization prevent advantageously the grain growth at the applied temperature.

[0040] The molding is preferably heated in step (a) in the decarbonizing atmosphere for about 2 to about 15 hours. The heating also takes place preferably for about 3.5 to about 12 hours and particularly preferably for about 4 to about 8 hours. [0041] The duration of the heating is selected in dependence upon the desired depth and/or the extent of the decarbonization in the surface edge layer. The time duration to be set also depends upon the molding. In a very compact molding with a large cross section is to be calculated a greater time duration because it takes longer until the entire molding has the temperature to be set after its introduction into the heating atmosphere. In moldings with a small cross section, such as, for example, in piston rings, a very good decarbonization occurs already after a heating of about 4 hours. For the expert it is, however, possible without problem to find a suitable time duration in

dependence upon the applied temperature and the molding whose surface edge layer is to be decarbonized.

[0042] It is particularly preferred if, in step (a), the molding has first for about 2 to about 12 hours

<u>/5</u>

a temperature that lies within a range between about 1000°C and about 1100°C, and then for about 0.5 to about 3 hours a temperature which lies within a range between about 850°C and about 1000°C.

[0043] It is also preferred if the temperature of the molding in step (a) amounts first for about 2 to about 12 hours to about 1050°C and then for about 0.5 to about 3 hours to about 950°C, in particular to about 920°C.

[0044] With regard to the time duration during which the moldings must be held before cooling at a somewhat lower temperature of about 850°C to 1000°C, a time duration of about 0.75 hours to about 1.5 hours, and in particular a time duration of about 1 hour, has shown to be advantageous. However, this time duration depends, as already explained, also from the cross section of the possibly compact molding. A compact molding with a large cross section is held for a longer time at the somewhat lower heating temperature in comparison with a compact molding of smaller cross section, so that the desired cooling of the molding to the somewhat lower temperature can take place.

[0045] It is advantageous if, in step (a), the decarbonizing atmosphere has a carbon level of about 0.15% by volume. Of course, however, also other carbon levels can be set in the decarbonizing atmosphere.

[0046] It is advantageous if the decarbonizing atmosphere has a specific carbon level so as to set a defined carbon content in the surface edge layer of the molding. In this way it is prevented that a complete decarbonization of the surface edge layer occurs. The residual content of carbon in the surface edge layer is insofar of advantage because the mechanical processing of the molding is facilitated.

[0047] The carbon level of the decarbonized atmosphere is set, for example, by setting a constant carbon level with the gases that constituted the decarbonizing atmosphere. The decarbonizing atmosphere can consist, for example, of CO, H_2 , and N_2 .

[0048] If the molding is heated in a decarbonizing atmosphere with a carbon level of 0.15% by volume and in dependence upon the time duration and the applied temperature, the carbon content of the surface edge layer lies between about 0.15% by weight and about 1.5% by weight. The residual carbon is available in the surface edge layer in the form of carbide.

[0049] It is also preferred to cool the molding in step (b) to a temperature between about 30°C and about 80°C. In a rapid cooling, that is, in a quenching of the molding is used a

quenching agent. However, in the sense of the invention, a quenching of the molding is not absolutely necessary after the step (a). As quenching agent can therefore be used any of the usual quenching agents, such as, for example, air, water, oil, a salt bath, a turbulent fluidized sand bed, et cetera. In the sense of the invention, the molding is preferably quenched and as quenching agent is preferably used oil.

[0050] It is also advantageous if, in step (b), the molding has a temperature of between about 400°C and about 650°C. It is even more preferred if the molding has a temperature of between 450°C and 600°C, most preferred a temperature of 550°C.

[0051] The annealing of the molding within the previously disclosed temperature range serves to ensure the tempering hardness. The annealing of the molding is, however, not absolutely necessary. An annealing of the molding can take place, for example, if, after the step (a), the molding is cooled not by quenching, but by slow cooling.

[0052] The annealing of the moldings (step (c)) takes place for a time period of about 0.25 to 2.5 hours, even more preferred for a time period of about 0.5 to about 2 hours, most preferred for a time period of about 1 hour. However, the annealing duration also depends upon the cross section of the possibly compact molding. A compact molding with a large cross section required naturally a longer annealing duration than a compact

molding with a smaller cross section, so that the molding has the temperature to be set overall and not only on the surface area.

[0053] It is also advantageous if the molding has up to step

(d) a temperature of between about 350°C and about 650°C,

preferably of between about 400°C and about 600°C, most

preferably of about 500°C. So that the properties of the

molding, for example, the strength and elasticity of piston

rings, are not changed too much in the core area during

nitriding, it is advantageous if the nitriding temperature is not

higher than the annealing temperature. The depth or the

thickness of the nitriding layer is fundamentally influenced by

the temperature applied during nitriding. In this way, the

thickness of the nitriding layer increases in a nitriding carried

out at a higher temperature.

[0054] It is very advantageous if, in step (d), the heating of the molding in the nitrogen-emitting medium takes place for a time period of about 2 to about 10 hours, preferably of 3 to 8 hours, even more preferably of 4 to 6 hours.

[0055] It is very advantageous when the composition of the iron-carbon casting material contains at least in part the above-mentioned nitride builders as alloy components. The decarbonized edge layer or the surface edge layer of the molding can be very well nitrided with regard to the possibly existing alloy components and

the no longer existing deposited graphite. The alloy components convert to the corresponding metal nitrides of the added metals and form in the molding a surface edge layer that is very resistant to abrasion.

[0056] The further object of the invention is attained by making available a molding produced in accordance with the process of the invention.

[0057] The molding of the invention can be produced accurately fitting and has a hardened surface or a hardened surface edge The accurately fitting production of the molding, which is now possible in accordance with the invention, leads to a large production yield. Insofar, the content of unuseable waste of the surface-hardened molding of cast iron is clearly reduced when compared to the molding produced in accordance with the conventional processes. The molding of the invention is also characterized by assimple and competitive production process. great economic advantage is therefore connected overall with the production of the molding in accordance with the invention. It is extremely advantageous if the molding is free of graphite and at least partially nitrided in a surface area layer extending from the surface of the molding into the interior of the molding. After step (a), this graphite surface edge layer has a depth of at least up to about 500 mm with reference to the

surface. That is, after the molding is treated in the decarbonized atmosphere, and before the molding is eventually further processed, the graphite-free surface edge layer has a depth of at least up to about 500 mm.

[0059] The molding produced according to the process of the invention has a surface edge layer after the post-processing with a depth of at least about 20 to up to about 500 mm with reference to the surface, in which no deposited graphite is present. These data refer to the end product, insofar it is clear that, insofar as no post-processing of the molding is required, wherein a part of the surface edge layer is removed regularly by the processing procedure, the surface edge layer without graphite deposition can have a greater depth, that is, a depth of up to 1.5 mm with reference to the surface.

[0060] It is highly preferred if the molding is nitrided in a surface edge layer at a depth with reference to the surface of at least up to about 20 mm.

[0061] These data refer to the post-processed end product.

However, also a nitriding hardness depth of at least up to 50 mm or of at least up to 100 mm can be reached. Under nitriding hardness depth is understood in the sense of the invention the surface edge layer in which the nitrogen diffuses during the nitriding and converts into nitrides with the casting material.

[0062] It is particularly preferred if the molding is a piston ring. The process of the invention allows the production of simple and economic accurately fitting piston rings of iron-carbon casting material with a uniform nitriding hardness depth.

[0063] It is also preferred to use the moldings of the invention in the production of tools, machines, motors, and/or automobile parts.

[0064] The expert knows that the moldings of the invention have multiple uses and cannot be limited to the examples shown The moldings produced from metastable solidified ironherein. carbon casting material can be used after the surface hardening according to the process of the invention everywhere where particularly edge layer properties with regard to an excellent abrasion, corrosion, and fatique endurance limit are particularly important. This is required, for example, in spur gears of drives, toothed wheels, crankshafts and camshafts, cylinder sleeves, et cetera. The moldings mentioned herein explicitly are to be understood, however, only as an exemplary enumeration. [0065] The expert understands that the process of the invention can be used everywhere where cast pieces were used until now, or where the use of cast pieces had been eliminated due to the defective surface edge properties.

[0066] The exemplary embodiment shown in the following does not limit the scope of the invention, but is to be understood merely as an example.

Exemplary Embodiment

Production of a Surface-hardened Piston Ring Produced According to the Process of the Invention

[0067] To produce a piston ring molded blank, cast iron material with the composition disclosed in Table 1 was poured under metastable solidification in a corresponding mold. The obtained piston ring molded blank, therefore, had a diameter of 84.4 mm and a ring thickness of 6.7 mm.

[0068] The piston ring molded blank was produced by using the sand casting process, so that the piston ring molded blank had the composition disclosed in Table 1 (residual content iron).

/7

Table 1

%C	%Si	%Mn	%P	%S	%Cr	%V	%Mo	%Ni	%Cu
3.0	2.0	0.6	0.05	0.03	0.5	0.2	0.02	0.1	0.1

[0069] The obtained piston ring molded blank was heated for 8 hours at $1050\,^{\circ}$ C and in a decarbonizing atmosphere with a carbon level of 0.15% by volume in a gas furnace. Therefore, the decarbonizing atmosphere had the following composition: 22% by volume CO, 42% by volume H₂, and 36% by volume N₂.

[0070] After the 8-hour heating of the piston ring molded blank at 1050°C, the temperature was reduced over a time period of 30 minutes to 920°C and then held for another hour at a temperature of 920°C. The piston ring molded blank was then quenched by transferring the piston ring molded blank into an oil bath and cooling the same to about 60°C.

[0071] To ensure the tempering hardness, the piston ring molded blank quenched in the oil bath was annealed for one hour at 550°C. After the annealing, the piston ring molded blank was cooled in the air. After the piston ring molded blank was completely cooled to the ambient temperature, the same was mechanically post-processed by contour turning. In this way were removed approx. 800 mm from the surface edge layer. The surface of the piston ring obtained in this way was free of graphite after the post-processing.

[0072] In addition, the piston ring was subjected to a pulsed plasma nitriding for surface hardening. The pulsed plasma nitriding was carried out at a temperature of about 500°C for six hours by using a gas mixture of N_2 , H_2 , and CH_4 . The piston rings were therefore stacked so that the nitriding took place merely on the bearing faces and on the inner diameter.

[0073] The piston rings produced according to the process of the invention have a graphite-free surface edge layer with a depth with reference to the surface of at least 50 mm as well as

a nitriding hardness depth, that is, a nitrided surface edge layer of at least 50 mm. In the core of the piston ring the graphite was deposited in the form of temper carbon.

Description of the Drawings

[0074] In Fig. 1 is shown for further clarification the temperature control in the previous exemplary embodiment in a temperature-time diagram. Fig. 1 shows a schematic illustration of the separate process steps I to V according to the exemplary embodiment. The numeric values in the diagram are therefore not entered according to scale. In the diagram, the time t is entered on the x-axis and the temperature T is entered on the y-axis.

I: Execution of the Edge Decarbonization and Carbide
Dissociation Annealing

The piston ring molded blank was heated for 8 hours at 1050°C in an atmosphere with a carbon level of 0.15% by volume. The piston ring molded blank was then cooled to a temperature of 920°C and held at this temperature for 1 hour.

II: Quenching

The piston ring molded blank was cooled rapidly in an oil bath from 920°C to 60°C.

III: Annealing

To ensure the tempering hardness, the piston ring molded blank was annealed for 1 hour at a temperature of 550°C.

IV. Mechanical Processing

After the piston ring molded blank was cooled to ambient temperature, it was post-processed mechanically by contour turning.

V. Nitriding

The post-processed piston ring was subjected for 6 hours at 500°C to a pulsed plasma nitriding in an atmosphere of N_2 , H_2 , and CH_4 .

<u>/8</u>

Patent Claims

- 1. A process for surface hardening a molding of metastable solidified iron-carbon casting material, wherein the process comprises the steps of:
 - (a) heating the molding in a decarbonizing atmosphere,
 - (b) cooling the molding, and
 - (c) heating the molding in a nitrogen-emitting medium.
- 2. The process of claim 1, wherein between the step (a) and the step (c) is provided another step (b1), in which an annealing of the molding takes place.

- The process of claim 2, wherein between the step (b1) and the step (c) is provided another step, in which a processing of the molding takes place.
- 4. The process of claim 1 to 3, wherein the metastable solidified iron-carbon casting material is a tempered cast.
- 5. The process of one of the claims 1 to 4, wherein, in the step (a), the molding has a temperature that lies within the range between about 700°C and about 1200°C.
- 6. The process of one of the claims 1 to 5, wherein, in the step (b), the molding is heated in the decarbonizing atmosphere for about 2 to about 15 hours.
- 7. The process of one of the claims 1 to 6, wherein, in the step (a), the molding has first for about 2 to about 12 hours a temperature that lies within the range between about 1000°C and 1100°C, and then for about 0.5 to 3 hours a temperature that lies within the range between about 850°C and about 1000°C.
- 8. The process of one of the claims 1 to 7, wherein, in the step (a), the decarbonizing atmosphere has a carbon level of about 0.15% by volume.
- 9. The process of one of the claims 1 to 8, wherein the molding is cooled in the step (b) to a temperature between about 30°C and about 80°C.

- 10. The process of one of the claims 1 to 9, wherein, in the step (b1), the molding has a temperature of about 400°C to about 650°C.
- 11. The process of one of the claims 1 to 10, wherein, in the step (b1), the annealing of the molding takes place for a time period of about 0.25 to 2.5 hours.
- 12. The process of one of the claims 1 to 11, wherein, in the step (c), the molding has a temperature of between about 350°C and about 650°C.
- 13. The process of one of the claims 1 to 12, wherein, in the step (c), the heating of the molding in the nitrogenemitting medium takes place for a time duration of about 2 to about 10 hours.
- 14. A molding produced in accordance with the process of one of the claims 1 to 13.
- 15. The molding of claim 14, wherein the molding is at least partially nitrided in a surface area layer extending from the surface of the molding into the interior of the molding.
- 16. The molding of claim 14 of 15, wherein, after the step (a), the graphite-free surface edge layer has a depth with reference to the surface of at least up to about 500 mm.
- 17. The molding of one of the claims 14 to 16, wherein the molding

- is nitrided in a surface edge layer in a depth with reference to the surface of at least up to about 20 mm.
- 18. The molding of one of the claims 14 to 17, wherein the ... molding is a piston ring.
- 19. A use of a molding of claims 14 to 18 in the production of tools, machines, motors, and/or automobile parts.

Fig. 1

